Offprinted from the *Journal of The Chemical Society, Faraday Transactions II*, 1977, Vol. 73.

# High and Low Frequency Torsional Absorptions in Nematic K21

BY GARETH J. EVANS

Chemistry Department, University College of Wales,
Aberystwyth, Dyfed, SY23 1NE

AND

MYRON EVANS*†

Physical Chemistry Laboratory, South Parks Road, Oxford, OX1 3QZ

*Received* 19*th July*, 1976

The far infrared absorption of 4 cyano-4′n-heptyl biphenyl (K21) has been measured in the nematic phase at 296 K in the frequency range 10-200 cm$^{-1}$. An incompletely resolved narrow band at 148 cm$^{-1}$ has been assigned to whole-molecule torsional oscillation on the evidence supplied by (*a*) dilution in cyclohexane, (*b*) application of an aligning field and (*c*) measurement of the f.i.r. intramolecular modes of 4-cyanobiphenyl, 4-n-heptyl biphenyl and biphenyl.

With a dipole moment aligned in the long axis, rotational absorptions may arise only from torsion about the mutually perpendicular short axes, an energetic process which is simulated here by an expansion of the orientational autocorrelation function in terms of successive memory functions. These are autocorrelation functions of the Langevin random torque, its time derivative, *etc.* Assuming that the latter decays exponentially (Markov process), equations for the dielectric loss, permittivity, and power absorption coefficient are deduced which describe the MHz absorption observed by Moutran in aligned nematic K21, and which upon extrapolation yield a narrow librational peak at 137 cm$^{-1}$, the result of an abnormally large mean square torque and an abnormally long residence at the bottom of deep and steep intermolecular potential wells.

In two recent studies [1, 2] of the far infrared and microwave absorptions of the molecular rotational dynamics in nematogenic and cholesteric mesophases, the results seem to indicate that torsional oscillation (libration) is very much easier about the long ($Z$) axis of the very anisotropic molecules than about the mutually perpendicular short axes. A corollary is that extreme anisotropy of molecular torsion in these phases could be used to investigate how well the far infrared librational peaks are simulated by current theories [3, 4] of brownian motion, based on Langevin's equation:

$$\dot{\boldsymbol{\omega}} = -\beta\boldsymbol{\omega}+\boldsymbol{\Gamma}(t). \tag{1}$$

Here, the molecular angular acceleration $\dot{\boldsymbol{\omega}}$ is ascribed classically to two sources, the retarding environmental " friction " $\beta$, proportional to the angular velocity, and a propagating torque per unit molecular moment of inertia $\boldsymbol{\Gamma}(t)$ that arises randomly from the same source. In a pseudo-crystalline nematogenic phase at any instant $t$, $\Gamma_z$ will be much smaller than $\Gamma_y$ or $\Gamma_x$, where

$$\boldsymbol{\Gamma} = \boldsymbol{i}\Gamma_x+\boldsymbol{j}\Gamma_y+\boldsymbol{k}\Gamma_z$$

in standard notation, since $\Gamma_y$ and $\Gamma_x$ will be the derivatives with respect to orientation of very large potential wells, at the bottom of which the molecules librate with a very restricted distribution of frequencies. Consequently the Debye critical

---

† present address: Chem. Dept., University College of Wales, Aberystwyth, Dyfed, SY23 1NE

frequency [5] occurs typically in the MHz range, [five or six decades below that of the far infrared (30-6000 GHz)]. This could be similated theoretically by eqn (1) *via* the well known Debye equations for loss and permittivity, but to do this is to take insufficient account of the fundamental fact that phenomena such as high frequency torsional oscillations of whole molecules, whatever their source and type, appear much the same statistically to low frequency probe fields, where they give rise to " Debye-type " loss curves, and exponential tailing of the orientational autocorrelation function.[6] Many different kinds of high frequency angular fluctuations become evident in the far infrared which are blurred and indistinguishable to fields at frequencies such as the MHz range. Thus it is not surprising that eqn (1), upon which Debye's theory of rotational diffusion is based, has to be generalised and made more realistic. It has to be able to simulate, *via* a continuous mathematical function of frequency, absorption *peaks* which may be separated by many decades. The deeper the energy wells within which the molecules librate, the greater would be this separation, a nematogen being an extreme case.

Recent approaches [7-10] to this problem have made use of an equation where the friction coefficient ($\beta$) is made frequency dependent. The orientational autocorrelation function [$c(t)$] may then be expressed in terms of a memory function $K$, which is itself the autocorrelation function of the torque. The linking equation is an integro-differential:

$$\dot{c}(t) = -\int_0^t K(t-\tau)c(\tau)\,\mathrm{d}\tau, \tag{2}$$

which, in view of the fact that $K$ is itself a correlation function, may be extended [11] to:

$$\frac{\partial}{\partial t}K_{n-1}(t) = -\int_0^t K_n(t-\tau)K_{n-1}(\tau)\,\mathrm{d}\tau. \tag{3}$$

This series has been truncated [7-10] at a level which: (*a*) does not introduce more than two zero-time averages $K_n(0)$; (*b*) fairly accurately reproduces far infrared and lower frequency absorptions or dispersions of small dipolar and non-dipolar molecules.

In this paper we use the nematogen 4-cyano-4′-n-heptyl biphenyl (K21) as the anisotropic rotator. Since this molecule has the permanent dipole moment aligned parallel to the long axis, rotational type absorptions may arise only from various torsions about the short axes. The low frequency loss peak in the parallel aligned nematic phase [12] is at 2MHz, and its variation with temperature indicates a very great barrier to rotational diffusion ($\sim 60\pm 8$ kJ mol$^{-1}$). The far infrared spectrum of nematogenic K21 has been measured here in an attempt to observe a sharp librational peak which could be assigned to the short time torsions of which the 2MHz peak is a manifestation when using low frequency probe fields. It is of interest to see what kind of absorption is predicted in the far infrared and MHz using a truncated Mori series of eqn (3).

## EXPERIMENTAL

The spectra presented here were measured at room temperature with a Grubb-Parsons/N.P.L. cube interferometer using amplitude modulation of the broad-band radiation reaching a Golay pneumatic detector. The interferograms were Fourier transformed digitally and the power absorption coefficient $\alpha(\bar{\nu})$ (neper cm$^{-1}$) calculated from the ratio of intensities penetrating two different sample thicknesses.

The sample itself was contained in a VC-01 cell with TPX windows, which were not pretreated in order to align the mesophase in any particular direction. With a maximum resolution of 2 cm$^{-1}$, the frequency range 10-200 cm$^{-1}$ was covered with two beam dividers.

Reproducibility between successive interferograms was about $\pm 5$ % of $\alpha(\bar{\nu})$. The systematic uncertainty [13] arising from convergent beam effects is minimal when using sample thicknesses such as ours : ~ 0.2 mm.

Sample purity was checked by observing the nematic–isotropic transition point with a polarising microscope ; other materials were prepared using techniques designed to minimise moisture impurity.

## RESULTS AND DISCUSSION

The spectrum of the nematogen at 296 K is illustrated in fig. 1 together with that of a 2.513 mol dm$^{-3}$ solution of *p*-cyanobiphenyl in dioxan and a 0.90 mol dm$^{-3}$ solution of biphenyl in cyclohexane. In fig. 2 are illustrated spectra of *p*-n-heptyl biphenyl and a dilute solution of K21 in cyclohexane. These are presented in an attempt to find which of the series of bands in K21 can be attributed to modes of internal vibration or bending, and which is the sharp absorption [14] corresponding to whole molecule torsional oscillation, if in fact it exists at all in this frequency region. We predict a sharp librational peak on the basis that this motion takes place in a pseudo-crystalline well-ordered environment, and against a large potential barrier. We are assuming in brownian theory that the torsion is that of a rigid ellipsoidal particle, whereas it is more probable that it would be coupled with intramolecular motions such as torsion of the two rings with respect to each other, and dynamical fluctuations in the n-heptyl tail.

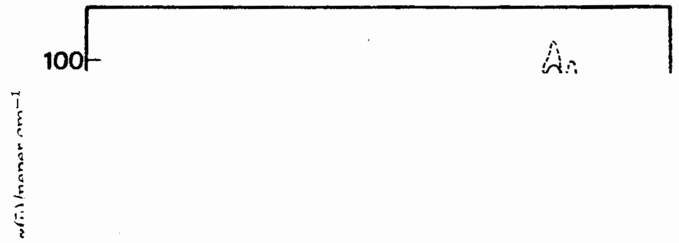
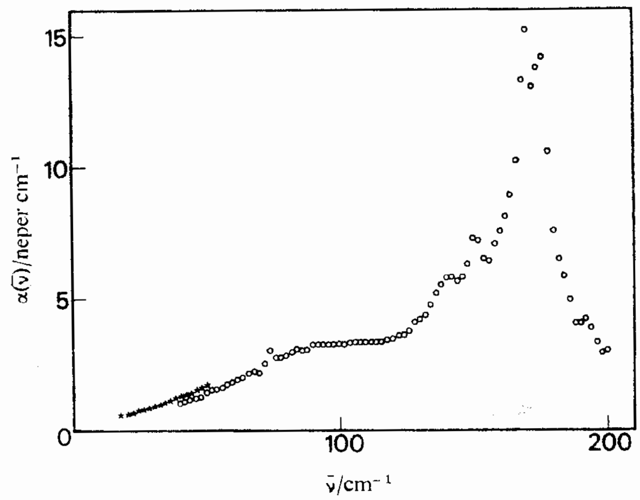


FIG. 1.—Far in ematic phase ;
(2) 2.513 mol d sorption ; (3)
0.9 mol dm$^{-3}$ t ıder a field of

The only are those at
148 and 17 1 is judged
to be intramolecular on the basis that this molecule is practically non-dipolar, the 110 cm$^{-1}$ peak shoulder present in the three other molecules being similarly discounted on the basis that it occurs in the non-polar biphenyl (fig. 3) and is probably an overtone due to some movement of the rings with respect to each other]. The application of an aligning D.C. field [1, 2, 12] of 7.1 kV cm$^{-1}$ perpendicular to the axis of the measuring beam shifts the 148 cm$^{-1}$ peak of K21 slightly to higher frequencies, and changes its intensity (fig. 1) relative to the group of bands around 170 or 180 cm$^{-1}$ ; whereas the 175 cm$^{-1}$ peak frequency seems to be unaffected. Dilution of K21 in cyclohexane destroys any nematogenic properties, and also changes markedly (fig. 2) the relative intensities of the 148 and 175 cm$^{-1}$ peaks, the former now being much less

pronounced. Thus it seems that both the application of a field and dilution (respectively increasing and decreasing environmental symmetry) have effects on the 148 $cm^{-1}$ peak which are distinctly different from those on the others present in the total spectrum. This peak is, therefore, taken as due to the high frequency torsional oscillation of the molecule as a whole about its short axes.



(*a*)

(*b*)

FIG. 2.—(*a*) Absorption of 0.08 mol $dm^{-3}$ K21 in cyclohexane at 296 K, corrected for solvent. ○ 50 gauge beam divider ; ★ 200 gauge beam divider ; (*b*) absorption of 0.05 mol $dm^{-3}$ *p*-n-heptyl biphenyl in cyclohexane at 294 K, corrected for solvent.

These qualitative remarks can be underlined by attempting to link this peak theoretically to the Debye absorption at 2 MHz. To do this we use a truncation of eqn (3) :[7-10]

$$K_1(t) = K_1(0) \exp(-\gamma t). \tag{4}$$

Here $K_1(t)$ is the autocorrelation function of the derivative of the random torque with respect to time and, by Doob's theorem,[6] eqn (4) implies that this must behave statistically as a Markov variable, whose future behaviour is unaffected by past events. $K_1(t)$ is the memory function of $K_0(t)$, which is itself the memory function of $c(t)$[eqn (2) and (3)]. It is known [15] that any earlier truncation such as:[8]

$$K_0(t) = K_0(0)\exp(-\gamma_0 t) \tag{5}$$

does not lead to a satisfactory description of the high frequency return to transparency of typical far infrared absorptions in isotropic fluids. Eqn (5) and variants [16] of such leads to $m/J$-diffusion, with $c(t)$ containing physically unrealistic coefficients of odd powers of time in its Maclaurin expansion. On the other hand, eqn (4), which leads to an asymptotic $\omega^{-4}$ dependence of $\alpha$ upon $\omega$ at high frequencies, has been used satisfactorily in several recent papers;[7-10] although the exponential $K_1(t)$ still has the drawback of not being even in time, as all classical correlation functions should be,[6] and of being incapable [17] of describing the dynamical transition to free rotor behaviour in the limit of vanishing torque. The Langevin-type equation implied from eqn (4) takes the form:

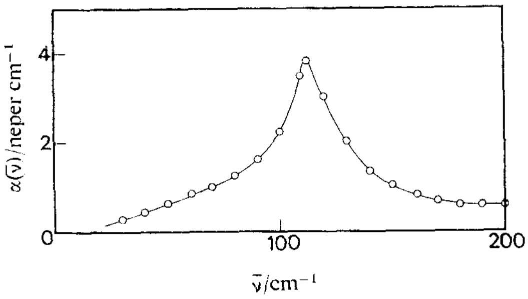


FIG. 3.—Absorption of 0.9 mol dm$^{-3}$ biphenyl in cyclohexane at 296 K corrected for solvent.

$$\frac{\mathrm{d}^2}{\mathrm{d}t^2}(\boldsymbol{\omega}\times\boldsymbol{u})+\gamma\frac{\mathrm{d}}{\mathrm{d}t}(\boldsymbol{\omega}\times\boldsymbol{u})+[K_0(0)+K_1(0)](\boldsymbol{\omega}\times\boldsymbol{u})+\gamma K_0(0)\boldsymbol{u} = \dot{\boldsymbol{\Gamma}}(t) \tag{6}$$

for a linear or spherical rotor. Here,

$$K_0(0) = \langle\dot{\boldsymbol{u}}^2(0)\rangle = \langle[\boldsymbol{\omega}(0)\times\boldsymbol{u}(0)]^2\rangle$$

$$K_1(0) = \frac{\langle\ddot{\boldsymbol{u}}^2(0)\rangle}{\langle\dot{\boldsymbol{u}}^2(0)\rangle}-\langle\dot{\boldsymbol{u}}^2(0)\rangle$$

where $\boldsymbol{u}$ is the dipole unit vector and $\boldsymbol{\omega}$ the angular velocity. The mean square angular velocity is $2kT/I_B$ for a linear or spherical top molecule, so that $K_0(0)$ is taken from the moment of inertia, while the mean square angular acceleration contains a centripetal component together with an intermolecular contribution proportional to the applied mean square torque, a measure of the slope of the potential energy surface. Solving eqn (2), (3) and (5) with the Heaviside expansion theorem yields $c(t) = \langle\boldsymbol{u}(0)\cdot\boldsymbol{u}(t)\rangle$ analytically in terms of $\gamma$, $K_0(0)$ and $K_1(0)$ as a sum of three complex exponentials. Fourier transformation yields the dielectric loss and permittivity as:

$$\varepsilon''(\omega) = \frac{(\varepsilon_0-\varepsilon_\infty)\omega\gamma K_0(0)K_1(0)}{\gamma^2[K_0(0)-\omega^2]^2+\omega^2\{\omega^2-[K_0(0)+K_1(0)]\}^2} \tag{7}$$

$$\varepsilon'(\omega) = \varepsilon_0-\frac{(\varepsilon_0-\varepsilon_\infty)\omega^2(\gamma^2[\omega^2-K_0(0)]+[\omega^2-K_1(0)]\{\omega^2-[K_0(0)+K_1(0)]\})}{\gamma^2[K_0(0)-\omega^2]^2+\omega^2\{\omega^2-[K_0(0)+K_1(0)]\}^2}. \tag{8}$$

These are related to the power absorption coefficient by:

$$\alpha(\nu) = \frac{2\sqrt{2}\pi\varepsilon''(\omega)\bar{\nu}}{\{[\varepsilon'^2(\omega)+\varepsilon''^2(\omega)]^{\frac{1}{2}}+\varepsilon'^2(\omega)\}^{\frac{1}{2}}} \tag{9}$$

with $\omega = 2\pi\bar{\nu}c$.

The equivalent of the Debye relaxation time ($\tau_D$) can be found in terms of $\gamma$, $K_0(0)$ and $K_1(0)$ in the limit $\omega\,(2kT/I_B)^{\frac{1}{2}} \to 0$ as:

$$\tau_D^2 = \frac{[K_0(0)+K_1(0)]^2-2K_0(0)\gamma^2}{K_0^2(0)\gamma^2}. \tag{10}$$

The loss and permittivity take up the classical Debye form [5] at low frequencies, and the least mean square fit of eqn (7) to Moutran's loss data [12] for aligned nematic K21 is shown in fig. 4. The optimum values are $K_0(0) = 0.26\times10^{24}\ \mathrm{s}^{-2}$; $K_1(0) = 668\times10^{24}\ \mathrm{s}^{-1}$; $\gamma = 0.51\times10^{12}\ \mathrm{s}^{-1}$, giving a calculated $\tau_D$ of 10 $\mu$s compared with an observed value [12] of 8 $\mu$s. The estimated value of the torque dependent $K_1(0)$ is at least an order of magnitude greater than the equivalent [8] in normal, isotropic, dipolar liquids, and $1/\gamma$ is an order longer. These results give a quantitative measure of the steep slope of the intermolecular potential energy surface, and of the very long decay time of the torque derivative, implying a long residence at the bottom of an energy well. Molecular torsional oscillation in the nematogen is an extremely fast process compared with the overall end over end rotational diffusion characterised by the Debye time $\tau_D$. The spectral consequences of this fast torsion may be simulated from eqn (9) by merely extrapolating the theoretical curve of fig. 4 to far infrared frequencies. This results in the narrow peak at 137 cm$^{-1}$ shown in fig. 5. We emphasize that this and the loss curve are manifestations of the same overall dynamical process, and are generated by the same, continuous mathematical function of frequency, the presence of one being an inevitable consequence of that of the other, although they may be separated, as here, by five or six decades. The total integrated intensity is constant and may be estimated by the sum rule of Gordon.[18] The high frequency resonance is almost exactly at $\omega^2 = K_1(0)$, and thus critically dependent on the uncertainty of this parameter. Since we extrapolate using the loss data, these determine the accuracy of $K_1(0)$.

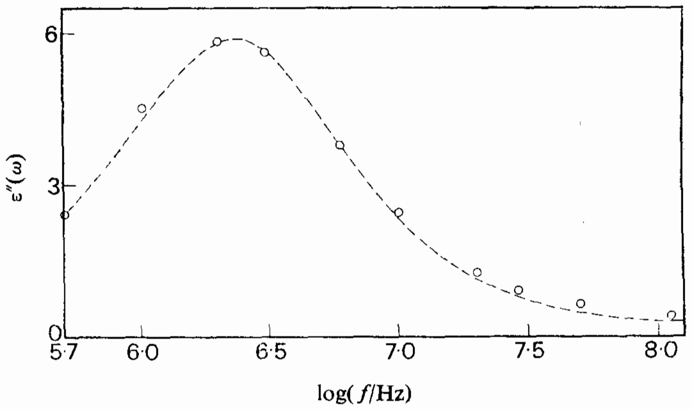


FIG. 4.—○ Measured loss (Moutran)[12] of magnetically parallel aligned K21 at 294 K. - - - Eqn (7), best fit by minimisation of squared residuals on ten measurements of $\varepsilon''(\omega)$.

Therefore, the rather simple eqn (6) produces a far infrared librational absorption with a peak frequency about 11 $\text{cm}^{-1}$ short of the 148 $\text{cm}^{-1}$ band assigned on the above evidence to an intermolecular origin. The theoretical peak is much too sharp, which means that $K_1(t)$ ought probably to take some form such as the non-Markovian:

$$K_1(t) = K_1(0) \sum_i f(\gamma_i, t) \tag{11}$$

rather than the primitive and restrictive simple exponential. In eqn (11) $f$ is ideally an even function of time, and physically it would mean that a spectrum of torque derivatives would be present in the ensemble, decaying at different rates and with a different statistical distribution from the Lorentzian of eqn (4). Naturally it is to be expected that a truncation of the series (3) at a later stage might also lead to a more realistic description, but this would be to introduce new functions $K_2(0), \ldots, K_n(0)$ and a multi-parameter model. Here, we have deliberately avoided this by using the earliest truncation commensurate with basic needs of fitting both experimental peaks.

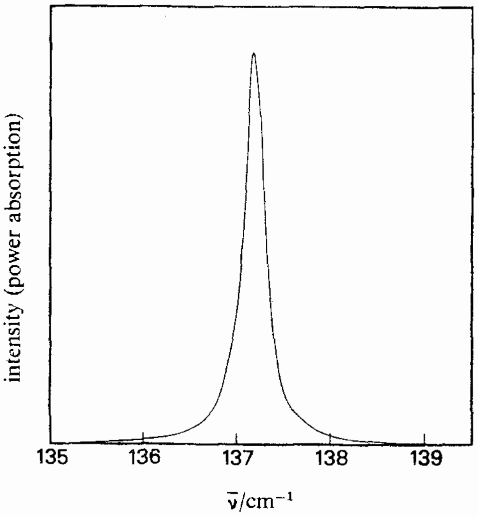


FIG. 5.—Eqn (9) with the parameters $K_0(0)$, $K_1(0)$ and $\gamma$ estimated from the fit of fig. 4 and given in the text.

We thank the S.R.C. for a studentship to G. J. E., and a fellowship to M. W. E., who also thanks the Ramsay Memorial Trust for the 1976-77 Fellowship.

[1] M. Evans, M. Davies and I. Larkin, *J.C.S. Faraday II*, 1973, **69**, 1011.
[2] M. Evans, R. Moutran and A. H. Price, *J.C.S. Faraday II*, 1975, **71**, 1854.
[3] R. Kubo, *Statistical Mechanics of Equilibrium and non-Equilibrium* (North Holland, Amsterdam, 1965).
[4] B. J. Berne and G. D. Harp, *Adv. Chem. Phys.*, 1970, **17**, 63.
[5] N. E. Hill, A. H. Price, W. E. Vaughan and M. Davies, *Dielectric Properties and Molecular Behaviour* (van Nostrand, London, 1969).
[6] A. Papoulis, *Probability, Random Variables and Stochastic Processes* (McGraw-Hill, N.Y., 1965).
[7] B. Quentrec and P. Bezot, *Mol. Phys.*, 1974, **27**, 839.
[8] G. J. Evans and M. Evans, *J.C.S. Faraday II*, 1976, **72**, 1169; G. J. Davies and M. Evans, *J.C.S. Faraday II*, 1976, **72**, 1194, 1206.

[9] D. Kivelson and P. Madden, *Mol. Phys.*, 1975, **30,** 1749.
[10] A. Gerschel, *Mol. Phys.*, 1976, **32,** 679.
[11] H. Mori, *Progr. Theor. Phys.*, 1965, **33,** 423.
[12] R. F. S. Moutran. *Thesis* (Univ. of Wales, 1975). M. Davies, R. Moutran, A. H. Price, M. S. Beevers and G. W. Williams, *J.C.S. Faraday II*, 1976, **72,** 1447.
[13] G. W. Chantry, *Submillimetre Spectroscopy* (Academic Press, London, 1971); G. J. Davies, *I.E.E.E.*, 1974, **IM-523,** 479.
[14] I. Darmon, C. Brot, G. W. Chantry and H. A. Gebbie, *Spectrochim. Acta*, 1968, **24*A*,** 1517; C. Brot and I. Darmon, *J. Chem. Phys.*, 1970, **53,** 2271.
[15] I. W. Larkin, *J.C.S. Faraday II*, 1974, **70,** 1457; M. Evans, *J.C.S. Faraday II*, 1975, **71,** 2051; 1976, **72,** 727.
[16] J. S. Rowlinson and M. Evans, *Ann. Rep.*, 1975, **72,** 5.
[17] G. J. Davies, G. J. Evans and M. Evans, *J.C.S. Faraday II*, 1976, **72,** 1901.
[18] R. G. Gordon, *J. Chem. Phys.*, 1965, **43,** 1307.

(PAPER 6/1416)

PRINTED IN GREAT BRITAIN AT
THE UNIVERSITY PRESS
ABERDEEN